DIASTEREO-SELECTIVITY OF DIELS-ALDER CYCLOADDITIONS OF ERYTHROSE BENZYLIDENE-ACETAL 1,3-BUTADIENES WITH MALEIMIDES

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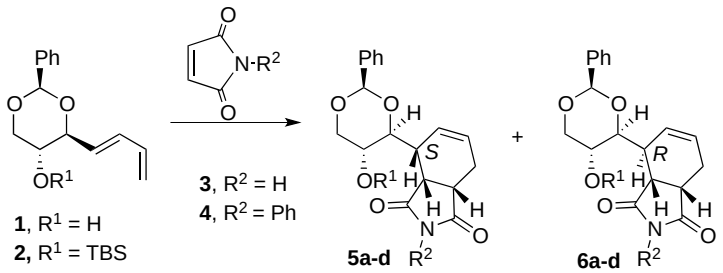
D-Erythrose benzydilene-acetal 1,3-butadienes **1**/ **2** were studied as partners in Diels-Alder cycloadditions with maleimides. Modest facial selectivity were found in non-catalysed reaction conditions between dienes **1**/ **2** and *NH*- (**3**)/ *N*-phenyl- (**4)** maleimides. The best chiral induction obtained was 3 (**5**): 1(**6**) and occurred at room temperature. However the diastereotopicity can be reversed raising the temperature; at 5ºC the major diastereomer is *R* configuration **6**, instead of **5**.



Scheme 1 – Four possible combinations of dienes **1**/**2** to maleimides **3**/**4** giving isomers **5**/**6**

An improvement of the facial selectivity occurs by tethering erythrose dienes and maleimides in bimetallic LACASA-DA cycloadditions. [1a,b] Figure 1 represents the *endo* approach of diene **1** and *NH*-maleimide that should occur to produce product **5a**. In approach **A** the reacting complex includes *R*-BINOL and approach **B** includes *S*-BINOL. The selectivity observed is complete in both cases giving the same product **5a** in moderate yields.

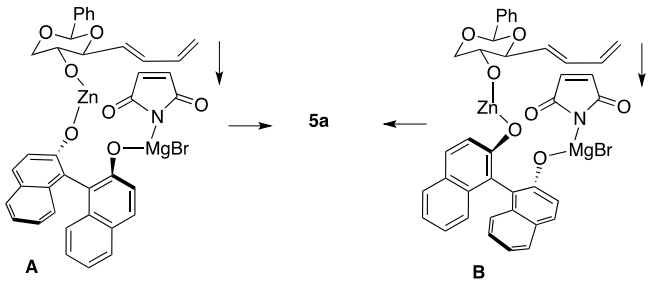


Figure 1 – Plausible approaches of erythrose diene **1** to *NH*-maleimide (**3**) in a Mg(II)/ Zn(II) complex with *S*- and *R*-BINOL

Acknowledgements: Thanks are due to FCT for project funding PTDC/QUI/67407/2006.

[1] a) Ward, D.E.; Souweha; M.S. *Org. Lett.* **2005**, 3533–3536. b) Ward, D.E.; Mohammad; S.A. *Org. Lett.* **2000**, 3937–3940.